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May 17, 2002

Mr. Daniel Greenbaum
Chairman, Clean Diesel Independent Review Panel
Health Effects Institute
955 Massachusetts Avenue
Cambridge, MA 02139

Dear Mr. Greenbaum:

As your panel undertakes its review of technologies for lowering sulfur levels in diesel fuel, I would like to provide some information on UniPure's breakthrough desulfurization process. We are in the final stages of developing and commercializing our alternative technology based on oxidation of the sulfur in diesel fuel. Our process has some unique technical and economic advantages compared to conventional technology.

UniPure's ASR-2 process produces ultra-low sulfur products having less than 5 ppm sulfur, and as low as 0.5 ppm, at very mild temperature and pressure without hydrogen and no fired heaters. The process steps are simple and straightforward, which means that scale-up will not entail much risk. The mild treatment avoids the undesirable side reactions that accompany hydrotreating. Accordingly, our process does not decrease diesel fuel lubricity. The capital and operating cost of the process is less than half that of a conventional hydrotreater. We have high confidence in our process because our development team is comprised of Ph.D. chemical engineers and a Ph.D. chemist having combined experience of about 120 years of process development with major oil companies.

Because of the simplicity, mild conditions and no need for hydrogen, it is feasible to build process units at small scale or large for application in refineries or as stand-alone units. We envision a unique application for dealing with the problem of fuel contamination in the product distribution system. We will offer small skid-mounted or truck-mounted units that can remediate off-specification contaminated highway diesel fuel at pipeline transfer stations or product terminals.

UniPure is building a 35 barrel-per-day pilot plant that will start operation later this year. We expect to have preliminary data by year end and a full licensing package available by early 2003. Many refiners and marketers of diesel fuel are beginning to indicate strong interest in our process, so we are optimistic that we can provide a cost-effective solution for ultra-low sulfur diesel production.

We would appreciate your considering UniPure's ASR-2 process as you develop your assessment. To provide you with additional information, I have attached an article that was presented at the AIChE 2002 Spring Meeting last March. Please don't hesitate to contact me if you require any additional information.

Sincerely,

Robert E. Levy
Sr. Vice President

cc: Ms. Mary Manners
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Paper No. 36c

UNIPURE'S OXIDATIVE DESULFURIZATION PROCESS CREATES NEW MARKET OPPORTUNITIES FOR SUPPLY OF ULTRA-LOW SULFUR FUELS

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Session on Non-Conventional Technology for Desulfurization

Introduction

North America and Europe are moving aggressively to introduce ultra-low sulfur transportation fuels, with sulfur levels of 10 to 50 ppm. Legislated deadlines for beginning the phase-in of these fuels are as early as 2005. In Germany tax incentives will begin driving the introduction of 10 ppm sulfur fuels in 2003. The requirements for ultra-low sulfur fuels are causing refiners, distributors and marketers to evaluate technology options that can meet the new regulations cost-effectively.

Last year UniPure announced a breakthrough process, based on oxidation chemistry. This novel process converts today's low sulfur gasoline and diesel fuel, in the range of 300 to 1500 ppm sulfur, to ultra-low sulfur at half the cost of a hydrotreater. Since then, UniPure, in partnership with Texaco, has developed improvements and enhancements to their ASR-2 process that reduce capital and operating cost and broaden the range of applications.

This presentation describes the technology, provides an update on the commercialization timetable and discusses the applications foreseen, including standalone plants.

UniPure Technology

UniPure's ASR-2 process converts diesel fuel and gasoline containing up to 1500 ppm sulfur, or higher, to ultra-low sulfur products having less than 5 ppm. The process is based on oxidation chemistry, which allows the reactions to be carried out at mild conditions: about 100 degrees C. and just enough pressure to contain the vapor. No hydrogen is required and the process has no fired heaters.

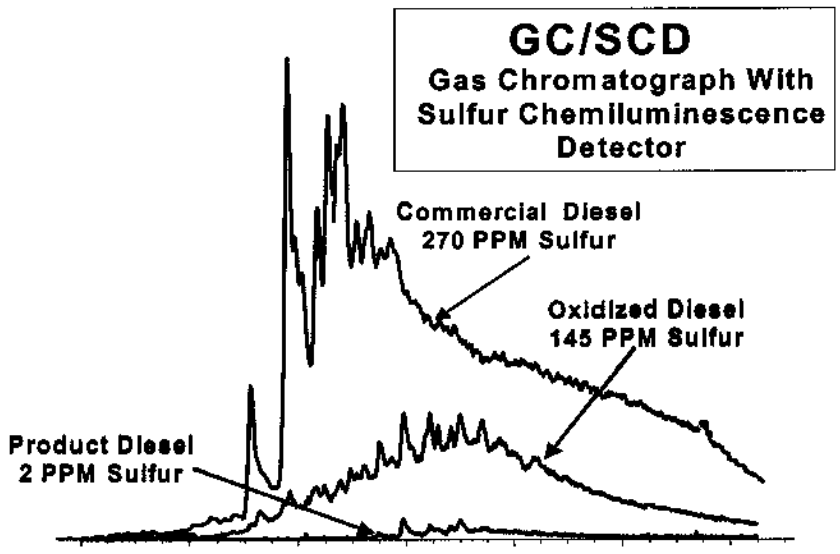
Oxidation of sulfur in hydrocarbons using hydrogen peroxide catalyzed by organic acid has been studied for over 30 years by many major oil companies and others (Aida 1993, Audeh 1994, Collins et al 1997, Freyermuth et al 1961, Heimlich & Wallace 1966, Herbstman & Patel 1982). The previous researchers proposed various processes, but none of them were found to be practical or economical until UniPure introduced its unique parameters. UniPure's technology allows the reactor to safely oxidize virtually 100 percent of the sulfur species in five minutes or less without oxidizing other species. When applied to naphtha or gasoline, the process does not oxidize the olefins, which means that the desulfurization is accomplished with no degradation of octane.

The desulfurization is achieved by removing the oxidized sulfur species, or sulfones, from the process by extraction. Because the feed normally has sulfur levels of no more than 1500 ppm, the amount of hydrocarbon removed with the sulfones is small. For a 500 ppm diesel fuel feed, the hydrocarbon extracted with the sulfones is about 0.3 percent of the feed. As a consequence of all of the sulfur species being oxidized, the product sulfur level reached is determined by the design and operation of the extraction step. UniPure has produced diesel fuel having less than 0.5 ppm (500 ppb) sulfur, which is probably the lowest sulfur diesel fuel ever produced from conventional petroleum.

We have demonstrated that this process is technically capable of desulfurizing feeds, such as straight-run diesel fuel, containing up to 10,000 ppm (1%) sulfur or more. Therefore, the limitation of 1500 ppm cited above is actually an economic issue. The amount of hydrogen peroxide oxidant required is proportional to the level of sulfur in the feed, so the operating cost increases accordingly. As a result, the acceptable feed sulfur limit for the process is actually determined by site-specific conditions. In some cases, desulfurization of streams having 2000 ppm sulfur or higher might be justified.

Gas chromatograph traces showing a typical diesel feed and desulfurization results are presented in Figure 1.

Figure 1.



Process Description

The process is comprised of three major steps: oxidation, extraction, and catalyst recovery, as shown in the simplified process flow diagram, Figure 2. The feed, in this case diesel fuel containing less than the current U.S. limit of 500 ppm sulfur, is introduced at 90-100 deg. C into the oxidation reactors, which are conventional stirred tank reactors. The reactors operate at low pressure, just sufficient to contain the vapors (about 1 bar for diesel and 3 bars for gasoline). The aqueous oxidizing solution comprising hydrogen peroxide, water, and recycled organic acid catalyst is also introduced co-currently into the reactors. The oxidation of the sulfur species, in this case mostly alkylated dibenzothiophenes, is completed within 5 minutes. The unique UniPure oxidizing solution compositions are such that the oxidation rate is fast, the oxidation is complete, the excess of peroxide used is small, and the spent acid solution simultaneously extracts about 50 % of the oxidized sulfur compounds. Thus, the oxidized diesel separated from the liquid-liquid separator following the oxidation step contains about half of the sulfur in the original feed. The sulfur in that stream is in the form of the corresponding alkylated dibenzothiophene sulfones. The rest of the oxidized sulfur is in the spent acid aqueous solution, which is processed further to reject the sulfones and regenerate the acid.

The oxidized diesel, which contains no residual peroxide, is washed with a small amount of water to recover the residual acid solubilized in it. Then, it is contacted with re-circulating aqueous caustic solution (NaOH) to remove any trace of acid, washed, and dried over salt to remove any trace of water.

The neutralized and dried oxidized diesel stream is then passed over a solid alumina adsorbing bed to extract the sulfones and yield an ultra-clean diesel product. Two alumina columns are operated in cycles. When one column is being used for adsorption of oxidized sulfur, the other column is being regenerated. The regeneration of the sulfone-loaded column is done in sequence by draining the retained diesel, washing with a lighter hydrocarbon stream, such as light naphtha or gasoline, drying off the naphtha, extracting with liquid hot methanol, and finally by drying off the methanol. The complete regeneration process is very fast. The methanol extract containing sulfones is then flash distilled to separate methanol for recycle and removal of the sulfones.

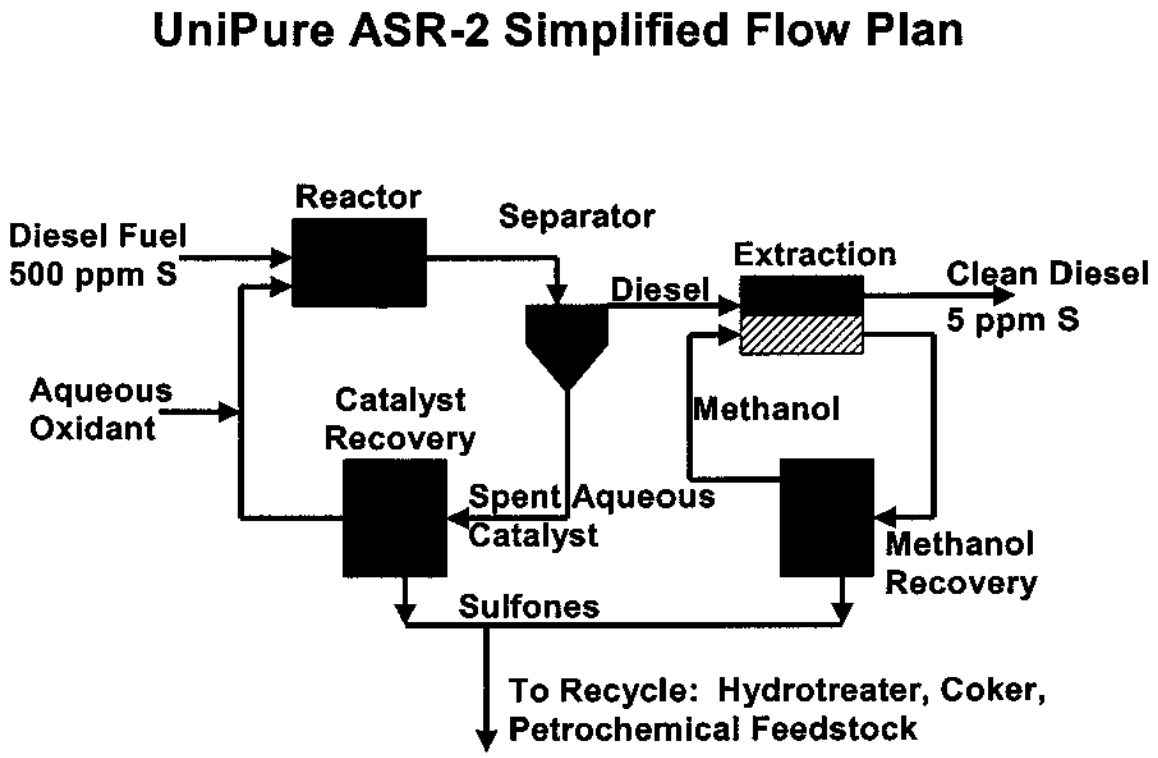
Mixed sulfones at purity in excess of 95 % can be recovered from the methanol extract of our process. In the case of a typical diesel fuel feed, the mixed sulfones are in a narrow range of C1-C5 alkylated dibenzothiophene sulfones. A suitable hydrocarbon stream, such as gasoil or diesel, is introduced into the methanol distillation step to receive the sulfones for their further disposition. Similarly, the gasoil or diesel is introduced into the flash distillation step of the spent acid stream from the separator (described above). This hydrocarbon then serves as a carrier stream for the rest of the sulfones that were extracted by the aqueous spent acid. The two sulfone carrier streams are combined for recycle or disposition.

There are a number of options available for the disposition of this small stream of sulfones, such as injection into a coker, feeding into a hydrotreater, disposal as a waste, or as raw material for specialty chemicals. UniPure is developing a broad range of solutions for the sulfones that are applicable whether the plant is installed in a refinery or on a stand-alone basis.

The spent acid is regenerated for recycling to the oxidation step by removing the amount of water required to maintain mass balance. The water that needs to be removed from the recycle loop balances the water introduced with the commercial hydrogen peroxide solution, water generated as an oxidation

by-product (peroxide to water), and the small amount of wash water used to recover acid soluble in the oxidized oil.

Figure 2



Process Development and Commercialization

The UniPure ASR-2 desulfurization process was developed jointly with Texaco, now ChevronTexaco, beginning early in 2000. The bench-scale development proceeded very rapidly and was carried out concurrently with engineering development of an optimized process flow plan. Texaco's engineering department generated material balances, an equipment list and capital and operating costs for a 25,000 barrel-per-day plant. We achieved highly favorable technical and economic results and now have initiated a pilot plant project at the scale of 35 barrels per day. The pilot plant will run both diesel fuel and gasoline feeds, beginning in the second quarter of 2002. UniPure expects to offer the process for license by third quarter.

UniPure is confident that this aggressive schedule for piloting and commercialization of the ASR-2 process is reasonable because the process complexity is low and the scale-up risks are minimal. This process operates at very mild conditions, has a simple CSTR reactor configuration, no heterogeneous catalysis considerations, no complex hydrodynamics and only two recycle streams. Each of the individual unit operations is straightforward and employs standard process equipment. As a result, we have not identified any significant scale-up risks or concerns.

Recent laboratory developments have identified several cost reduction opportunities, which will be tested in the pilot plant in the second half of 2002. These include improvements in the recovery of water from spent acid, in materials of construction and in extraction of sulfones from the hydrocarbon stream. The improvements will favorably impact both capital and operating cost, specifically energy consumption.

Product Quality

The UniPure ASR-2 process treats fuels with a light touch, as opposed to hydrotreating, which applies an intense treatment and results in many side reactions. The ASR-2 products are virtually unchanged in any properties other than sulfur. Even in the case of highly olefinic naphtha streams, the olefins are largely untouched, which means that octane number is not impacted. Samples of a commercial diesel fuel before and after treatment by the ASR-2 process were tested by Core Laboratories, who verified that all diesel quality specifications were satisfied. These results also confirmed that there were no significant quality changes in any properties other than sulfur content. Comprehensive product quality testing will be conducted in the second quarter of 2002 with samples generated by the pilot plant.

The ability of this process to routinely achieve extremely low sulfur levels, such as 2 ppm, as well as to produce a water-white diesel product, suggests that a high quality ultra-low sulfur diesel fuel could be marketed, which could command a premium price.

Economic Advantage

The estimated capital cost for a 25,000 barrel-per-day ASR-2 plant processing diesel fuel with 500 ppm sulfur to 5 ppm sulfur product is about $25 million, or $1000 per barrel of installed capacity. This is less than half the capital cost of a high pressure hydrotreater in similar service. The combination of amortized capital plus operating cost for this same 25,000 barrel-per-day ASR-2 plant is about 3.5 cents per gallon, which again compares very favorably with hydrotreating. The Department of Energy (US DOE 2001) estimated marginal hydrotreating costs for 500 ppm sulfur diesel being converted to 7 ppm product to be in the range of 4.7 to 9.2 cents per gallon. Another study by Charles River Associates (Moncrieff et al 2000) showed the incremental refining cost (based on hydrotreating) for diesel fuel in the U.S. to range from very low, for refineries already having high pressure hydrotreaters, to as high as 15 cents per gallon for refiners having no hydrotreating or hydrogen generation capabilities. Most of the refiners studied have incremental costs in the range of 5 to 8 cents per gallon.

UniPure's process also has a huge advantage over hydrotreating in energy consumption and greenhouse gas emissions. We estimate that ASR-2 emits no more than 20% as much carbon dioxide as a typical hydrotreater in equivalent service.

UniPure's process will be attractive for refineries with low pressure hydrotreaters, which cannot be retrofitted to achieve ultra-low sulfur levels, and for those with no existing hydrotreating capability. Because of the simplicity of the ASR-2 process, it is also feasible to build stand-alone plants for processing low sulfur (up to 1500 ppm) diesel and gasoline to ultra-low sulfur levels, or for installation near product terminals for re-processing off-spec or contaminated products.

Improvements to the UniPure process, which will be piloted in the second half of 2002, will further reduce the cost below 3.5 cents per gallon. Not only will these improvements lower the capital and

operating costs, they will extend the economically attractive range to higher levels of sulfur in the feed. They will also simplify the small-scale plants for convenient stand-alone applications.

Applications in Refineries

The UniPure ASR-2 process would be an obvious option for those refiners not having existing hydrotreaters for naphtha or diesel fuel. In these cases, the UniPure unit would process straight-run or cracked feedstocks. Although the process can readily handle feeds with sulfur levels up to 10,000 ppm (1%), the cost of the oxidant would be prohibitive. For economic processing, the maximum feed sulfur would be limited to perhaps 1500 ppm. Although the maximum train size for these units has not yet been studied in detail, the simplicity of the reactors and other unit operations suggests that large-scale plants in the range of 25,000 to 50,000 barrels per day could be built as single trains.

For refiners having existing low pressure hydrotreaters, or hydrotreaters that cannot be inexpensively retrofitted to produce ultra-low sulfur levels, an ASR-2 unit could be attractive for post-treating the effluent from the existing unit. The UniPure unit enables the existing hydrotreater to be debottlenecked and optimized to meet all product quality requirements. Since the ASR-2 unit effectively removes sulfur with feeds up to 1500 ppm, the existing hydrotreater can relax its desulfurization requirements. This can allow the hydrotreater to handle additional throughput, if so desired. Additionally, the existing unit can be configured to optimize aromatics saturation or other properties by changing the catalyst and operating conditions, letting the desulfurization be handled downstream in the ASR-2 process.

Applications as Stand-alone Plants

Significant shortages in supply are forecasted in both North America and Europe as ultra-low sulfur diesel fuel is introduced. Opportunities will exist to build stand-alone ASR-2 plants to process imported diesel stocks having 100 to 1500 ppm sulfur that could be purchased at favorable prices. These plants will take advantage of the ability to build UniPure units at sites remote from refinery infrastructure. Accordingly, they could be installed domestically, or at offshore locations, such as the Caribbean, to serve the U.S. market, or in Russia or the Middle East, to serve the European market.

There will also be opportunities to profitably operate domestic stand-alone plants that would serve one or multiple refineries by desulfurizing gasoline or diesel fuel more economically than hydrotreaters operating inside the refinery fence.

Applications at Product Terminals

As fuels having 10 to 30 ppm sulfur are moved through distribution systems to product terminals and on to consumers, there will be many opportunities for contamination from higher sulfur products. This will result from tank heels, residual products in transfer lines, leakage, and a variety of transportation-related situations. Ships, barges, tank trucks and pipelines will all contribute to the sulfur contamination problem, resulting in off-spec fuels in the product terminal tanks. Shared distillate product pipelines, which carry the majority of the transportation fuels in North America, create special concerns because of the difficulty in identifying the product interface quickly enough to avoid significant contamination by higher sulfur products that either precede or follow the ultra-low sulfur material.

Until now, the pipeline operators, terminal operators and marketers have foreseen no satisfactory options for dealing with the off-spec fuels that are certain to occur, other than to downgrade them to lower value products. However, small UniPure ASR-2 plants can be built adjacent to product terminals, or as regional plants serving several terminals. These units will be able to process sulfur-contaminated off-spec fuels and return them on specification to the terminal. This is a totally new application for desulfurization technology that will solve one of the thorny problems facing the introduction of ultra-low sulfur fuels. This approach also will enable the terminal operators and marketers to maintain attractive margins.

Recognizing that most terminal operators would not be interested in operating a process unit, we envision that separate business entities would build, own and operate these plants. They would process off-spec fuels on a tolling basis across the fence. We are also developing the design of skid-mounted and truck-mounted units to facilitate the servicing of fuels at product terminals. UniPure intends to bring a total ultra-low sulfur fuel solution to the terminal operators, including sulfur interface detection, tankage guidelines, operating procedures and re-processing of contaminated products.

Conclusions and Implications

UniPure has developed a breakthrough process for ultra-low sulfur diesel fuel and gasoline, which will be commercialized in the third quarter of 2002. This novel process is less than half the cost of hydrotreating facilities in similar service and will have significant market opportunities in conventional refining applications, stand-alone plants and polishing units handling off-spec fuels at product terminals. UniPure looks forward to sharing the data from our pilot plant with potential early adopters of the ASR-2 process.

References

Aida, Tetsuo (Kinki University, Japan), "Method of Recovering Organic Sulfur Compound from Liquid Oil," European Patent Application No. 93302642.9, Filed April 4, 1993

Audeh, Costandi A. (Mobil Oil Corp), US Patent 5,310,479, May 10, 1994 (Process for Reducing the Sulfur Content of a Crude)

Collins, Frances M., Lucy, Andrew R, and Sharp, Christopher (BP Chemicals): "Oxidative Desulfurization of Oils Via Hydrogen Peroxide and Heteropolyanion Catalysis", Journal of Molecular Catalysis A: Chemical 117 (1997) 397-403

Freyermuth, Harlan B., et al, (General Aniline and Film Corp), US Patent 3,005,852, Oct. 24, 1961 and 3,006,963, Oct 31, 1961 (Production of Sulfoxides and Sulfones)

Herbstman, Sheldon and Patel, Jitendra (Texaco) "Oxidative Desulfurization of Residual Oils," Symposium on Upgrading of Synthetic Crudes, American Chemical Society, Kansas City, September 12-17, 1982

Heimlich, B.N. and Wallace, T.J. (Esso Research & Engineering), "Kinetics and Mechanism of the Oxidation of Dibenzothiophene in Hydrocarbon Solution," Tetrahedron, Vol. 22, pp3571-3579, Vol. 22, 1966, Pergamon Press Ltd.

Moncrieff, T.I., Montgomery, W.D., Ross, M.T., Ory, R.E., and Carney, J.T., "An Assessment of the Potential Impacts of Proposed Environmental Regulations on U.S. Refinery Supply of Diesel Fuel", Charles River Associates Report No. D02316-00, Prepared for American Petroleum Institute, August, 2000

U.S. Department of Energy, Energy Information Administration, "The Transition to Ultra-Low-Sulfur Diesel Fuel: Effects on Prices and Supply", May 2001